

Predicting trace metal solubility and fractionation in urban soils from isotopic exchangeability.

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ABSTRACT

Metal-salt amended soils (MA, n = 23), and historically-contaminated urban soils from two English cities (Urban, n = 50), were investigated to assess the effects of soil properties and contaminant source on metal lability and solubility. A stable isotope dilution method, with and without a resin purification step, was used to measure the lability of Cd, Cu, Ni, Pb and Zn. For all five metals in MA soils, lability (%E-values) could be reasonably well predicted from soil pH value with a simple logistic equation. However, there was evidence of continuing time-dependent fixation of Cd and Zn in the MA soils, following more than a decade of storage under air-dried conditions, mainly in high pH soils. All five metals in MA soils remained much more labile than in Urban soils, strongly indicating an effect of contaminant source on metal lability in the latter. Metal solubility was predicted for both sets of soil by the geochemical speciation model WHAM-VII, using E-values as an input variable. For soils with low metal solution concentrations, over-estimation of Cd, Ni and Zn solubility was associated with binding to the Fe oxide fraction while accurate prediction of Cu solubility was dependent on humic acid content. Lead solubility was most poorly described, especially in the Urban soils. Generally, slightly poorer estimation of metal solubility was observed in Urban soils, possibly due to a greater incidence of high pH values. The use of isotopically exchangeable metal to predict solubility is appropriate both for historically contaminated soils and where amendment with soluble forms of metal is used, as in toxicological trials. However, the major limitation to predicting solubility may lie with the accuracy of model input variables such as humic acid and Fe oxide contents where there is often a reliance on relatively crude analytical estimations of these variables.

Capsule:

Trace metal reactivity in urban soils depends on both soil properties and the original source material; the WHAM geochemical model predicts solubility using isotopically exchangeable metal as an input.

1. INTRODUCTION

Accurate assessment of risk from heavy metal contamination of the environment requires consideration of metal ‘reactivity’ or ‘lability’ in soils (Fairbrother et al., 1999; Lock and Janssen, 2001). Published literature (Degryse et al., 2004, Tack, 2010, Hammer et al., 2006) generally suggests that the lability of trace metals in soils is the net result of three factors: (i) soil properties, including soil physicochemical characteristics such as pH (e.g. McBride et al., 2006; Bonten et al., 2008) and redox potential (Borch et al., 2010) and the proportions of soil constituents such as Fe/Mn hydroxide and organic matter present (Tipping et al., 2003; Rodrigues et al., 2010); (ii) metal sources, which may vary greatly in their intrinsic metal lability (e.g. Atkinson et al., 2011; Mao et al., 2014) and (iii) soil-metal contact time, because there is a time-dependency to both metal fixation in soils (e.g. Tye et al., 2003; Ma et al., 2006b) and the release of trace metals from contaminant sources in soils (Kaste et al., 2006; Atkinson et al., 2011). Generally, low metal lability is more likely in soils with high pH values and following long contact times. Recent studies have focused on the concentrations and origins of heavy metals in the urban environment (Manta et al., 2002; Cheng et al., 2014; Wei and Yang, 2010), but the effects on lability arising from characteristics of the original contaminant source are usually difficult to assess (Mao et al., 2014).

A range of techniques have been developed to measure the lability of trace element fractions in soils, among which isotope dilution is perhaps the most appropriate method (Degryse et al., 2009). This approach defines an amount of metal, distributed between the solution and solid phases, which is isotopically exchangeable, known as the E-value or M_E (Smolders et al., 1999; Young et al., 2000). Measurement is achieved by adding a small ‘spike’ of an enriched isotope of the analyte of interest into a pre-equilibrated soil suspension and measuring the isotopic abundance of the spike isotope in the separated solution phase. The extent to which the spike isotope has been able to mix with the indigenous soil metal quantifies the ‘isotopically exchangeable’ metal pool in the soil. The method has been modified to correct for the presence of non-labile metal in sub-micron colloidal particles (SCP-metal) by adding a resin purification step (Lombi et al., 2003). E-values can then be used as input variables to geochemical speciation models, such as WHAM (Windermere Humic Aqueous Model, Tipping et al., 2003) to predict metal fractionation and speciation in the solid and solution phases of soils respectively (Tipping et al., 2003; Shi et al., 2008; Almas et al., 2007; Buekers et al., 2008b; Marzouk et al., 2013b).

The primary aims of this study were to investigate how trace metal *lability* and *solubility* are affected by (i) soil properties, (ii) ageing and (iii) variable contamination sources in urban soils. To achieve this, objectives focussed on determination of the isotopically exchangeable fractions of Cd, Cu, Ni, Pb and Zn (M_E) in two distinct sets of soil samples. These included (i) soils, chosen for their range of land uses and soil properties, that had been incubated with metal nitrate salts (Cd, Cu, Ni, Pb and Zn) for several years and (ii) urban contaminated soils, from Nottingham and Wolverhampton (UK), chosen for their range of metal contaminant concentrations and sources. To reveal the effect of contaminant source, the ‘lability’ of soils from the two datasets were compared by normalising values of % M_E against soil pH;

72 logistical models for describing metal lability with pH were parameterised. Secondary objectives
73 included: (i) testing for non-labile SCP-metal ($<0.22 \mu\text{m}$) by comparing values of M_E with equivalent
74 values following a resin cleaning procedure (M_{Er}); (ii) testing for metal *fixation* in air dried soil stored
75 for more than a decade, (iii) comparing a sequential fractionation scheme with fractionation by isotopic
76 exchangeability and (iv) assessing the performance of the geochemical model, WHAM VII, to predict
77 Cd, Cu, Ni, Pb and Zn solubility in both sets of soils.

78

79 **2. MATERIAL AND METHODS**

80 **2.1 Soil sampling**

81 Two sets of soils were used in this study. The first set comprised 23 metal-amended topsoils (MA soils),
82 from sites with contrasting land uses and parent material, to provide a wide range of soil properties (pH,
83 soil organic matter, mineral (hydr)oxides content and texture). These soils were collected for a previous
84 study of trace metal fixation and solubility (Tye et al., 2003; Tye et al., 2004) and had been amended
85 with metal nitrate salts to the limits prescribed by the UK Sludge Regulations (MAFF, 1993) ($\text{Cd} = 3$,
86 $\text{Cu} = 135$, $\text{Ni} = 75$, $\text{Pb} = 300$ and $\text{Zn} = 300 \text{ mg kg}^{-1}$) before being incubated at 16°C and 80% field
87 capacity (FC) for ~ 3 years (Tye et al., 2003), air-dried, and then stored for ~ 12 years prior to the current
88 study. The second set (Urban soils) consisted of 50 topsoils collected in the cities of Wolverhampton
89 (WV) and Nottingham (NG), UK. Site selection included consideration of historical and recent
90 industrial and domestic land use and locations included brownfield sites, rail transport sidings, urban
91 roadsides, waste disposal facilities, recreational areas, gardens, urban nature reserves and woodland and
92 parkland areas. Data relating to these soils has been published previously in an investigation of metal
93 speciation and bioavailability in risk assessment (Thornton et al., 2008; Hough et al., 2005).

94 **2.2 Soil characterization**

95 Some of the soil properties originally determined were re-measured to identify changes during storage
96 and to provide a more complete input dataset for subsequent modelling (Section 2.6). Soil pH was
97 measured on suspensions (1 g soil: 30 mL of 0.01 M $\text{Ca}(\text{NO}_3)_2$) using a pH meter with combined
98 Ag/AgCl glass electrode (Model pH 209, HANNA Instruments, Bedford, UK). Total organic matter
99 content was estimated using a LECO combustion analyser (Tye et al., 2003) for MA soils. For Urban
100 soils total organic matter content was calculated from the difference between total soil carbon (SC)
101 content measured using an Elemental Analyser (CE Instruments model Flash EA1112) and calibrated
102 using a range of certified soils, and carbonate content determined by manometric assay using the Collins'
103 calcimeter method (Piper, 1954). Alkaline extraction was used to determine humic acid (HA) and fulvic
104 acid (FA) content in all soils. Organic carbon content in HA and FA was measured using a Shimadzu
105 TOC-Vcp analyser. Clay content (%) was estimated from the soil texture classification provided by
106 Tye et al. (2003) for MA soils. Iron, Al and Mn oxide concentrations were determined following
107 extraction with a mixture of sodium dithionite, sodium citrate and sodium bicarbonate (DCB extraction,

108 Anschutz et al., 1998). Total Cd, Cu, Ni, Pb and Zn concentrations in soil were determined following
109 digestion of 200 mg of finely ground soil with HF (40% AR), HNO₃ (70% TAG), HClO₄ (70% AR)
110 and 2.5 mL H₂O in a block digester (Model A3, Analysco Ltd, Chipping Norton, UK). Iron, Al and
111 Mn in DCB extractants and trace metals in acid digests were analysed by Inductively Coupled Plasma-
112 Mass Spectrometry (ICP-MS; Thermo-Fisher Scientific X-Series^{II}) operating in ‘collision cell mode’
113 (7% hydrogen in helium) to reduce polyatomic interferences.

114 **2.3 Cadmium, Cu, Ni, Zn, and Pb lability measured by isotopic dilution (E-value)**

115 *Sample preparation*

116 The stable isotopic dilution method used in this study was adapted from Atkinson et al. (2011). Soils
117 were pre-equilibrated in 0.01 M Ca(NO₃)₂ (1 g: 30 mL) on an end-over-end shaker for 3 days; 4
118 suspensions were made for each soil. An aliquot (0.4 mL) of enriched stable isotope stock solution
119 (ISOFLEX, San Francisco CA, USA) in ~2% HNO₃, with known isotopic abundances (IA) for ¹⁰⁸Cd
120 (IA = 69.7%), ⁶⁵Cu (IA = 99.0%), ⁶²Ni (IA = 98.2%), ²⁰⁴Pb (IA = 98.8%) and ⁷⁰Zn (IA = 92.7%) was
121 added to two of the suspensions and the other two were used as control samples to derive the natural
122 isotopic abundance of the labile metal. The spike isotopes used were, with the exception of ⁶⁵Cu, chosen
123 because they have relatively low natural isotopic abundance (De Bievre and Barnes, 1985). Therefore,
124 only a small addition to the system was required to produce a significant increase in IA from the
125 background level. To reduce the number of individual operations and to avoid adding different amounts
126 of isotopes to each soil, the samples were classified into several groups according to their soil metal
127 content. The level of isotope tracer to be added was determined from the highest concentration of metal
128 in each group to ensure that the difference in isotopic ratio between the spiked and un-spiked samples
129 was at least 20 %. After spiking, the suspensions were shaken for a further 3 days; the solution and solid
130 phases were then separated by centrifugation (2200 g) and then filtration (< 0.2 μm). For several Urban
131 soils, where the native and/or spike metal concentrations in 0.01 M Ca(NO₃)₂ suspension were judged
132 to be too low to provide reliable isotopic ratios (Midwood, 2007), a suspending solution of 1×10⁻⁵ M
133 EDTA was used to shift the labile metal equilibrium in favour of the soil solution while presenting
134 minimal risk of mobilizing non-labile metal, as shown by Atkinson et al., (2011) and Nazif et al., (2015).

135 *ICP-MS settings for measuring isotopic abundances and calculation of E-value*

136 Isotopic ratios in supernatant solutions were measured by ICP-MS in ‘collision cell with kinetic energy
137 discrimination’ (CCT-KED) mode to avoid interference from the chlorine dimer (³⁵Cl-³⁵Cl), and other
138 polyatomic species, on ⁷⁰Zn (Malinovsky et al., 2005; Stenberg et al., 2004). Quadrupole dwell times
139 were short to reduce plasma flicker: ¹⁰⁸Cd (10 ms), ¹¹¹Cd (2.5 ms), ⁶³Cu (2.5 ms), ⁶⁵Cu (10 ms), ⁶⁰Ni
140 (2.5 ms), ⁶²Ni (10 ms), ²⁰⁴Pb (10 ms), ²⁰⁶Pb (2.5 ms), ²⁰⁷Pb (2.5 ms), ²⁰⁸Pb (2.5 ms), ⁶⁶Zn (2.5 ms) and
141 ⁷⁰Zn (10 ms). The isotopes ⁵⁹Co, ¹⁰⁷Ag and ²⁰²Hg were also measured, as quadrupole settle points
142 (Marzouk et al., 2013a). It is well known that the relative abundance of Pb isotopes varies according
143 to the sources of Pb present in the soil (Komarek et al., 2008). Therefore, instead of relying on assumed

144 relative abundances of naturally occurring isotopes, the apparent isotopic ratio in un-spiked samples
 145 (blanks) was also determined for all five elements. To avoid the electron multiplier detector tripping to
 146 analogue mode, all the sample solutions were diluted appropriately.

147 A source of error when analysing stable isotopes is mass discrimination: isotopes with greater mass are
 148 measured by ICP-MS with greater sensitivity and so the measured ratio of CPS for two isotopes is not
 149 equal to their true isotopic ratio. External mass discrimination correction was therefore applied using a
 150 certified isotopic standard reference material (NIST, SRM 981) for Pb and a mix of single ICP-MS
 151 calibration standards for Cd, Cu, Ni, and Zn. The mixed standard (25 µg L⁻¹) was used to calculate a
 152 correction factor (K-Factor) (**Eq. 1**):

$$153 \quad K - factor = \frac{IR}{CR} \quad (1)$$

154 where IR and CR are the true isotopic ratio and the measured ratio of CPS for the isotopic standard
 155 respectively. For individual samples, the K-factor for each isotopic ratio (e.g. ²⁰⁴Pb/²⁰⁸Pb, ²⁰⁶Pb/²⁰⁸Pb,
 156 ²⁰⁷Pb/²⁰⁸Pb) was estimated by linear interpolation between the K-factor measured for standards run at
 157 intervals of eight samples.

158 Concentrations of isotopically exchangeable metal (M_E; mg kg⁻¹) were calculated for Cd, Cu, Ni, Pb
 159 and Zn from **Eq. 2** adapted from Gabler et al. (1999):

$$160 \quad M_E = \left(\frac{Am_{Msoil}}{W} \right) \left(\frac{C_{spk} V_{spk}}{Am_{Mspk}} \right) \left(\frac{spk IA_{spike} - bg IA_{spike} R_{ss}}{bg IA_{soil} R_{ss} - spk IA_{soil}} \right) \quad (2)$$

161 where Am_{Msoil} and Am_{Mspk} are the average atomic masses of Cd, Cu, Ni, Pb or Zn in the soils and the
 162 spike isotope solution respectively, W is the weight of the soil (kg), C_{spk} is the gravimetric concentration
 163 of the metal in the spike solution, V_{spk} is the volume of spike added (L), IA is the isotopic abundance
 164 and R_{ss} is the ratio of isotopic abundances, spiked (spk): background (bg), for the two isotopes in the
 165 spiked soil solution. For comparative purposes, lability is often expressed as a percentage of the total
 166 metal content of the soil (%M_E)

167 A ‘resin purification’ test for the presence of non-labile metal in suspended colloidal particles (SCP-
 168 metal; < 0.2 µm), first described by Lombi et al. (2003), was undertaken. Analytical grade Na-Chelex-
 169 100 resin (Bio-Rad laboratories, UK) was converted to the Ca²⁺ form by equilibrating in 0.5 M Ca(NO₃)₂
 170 for 2 hours. The resin was then washed twice with MilliQ water (18.2 MΩ cm) to remove remaining
 171 Na⁺ ions. An aliquot of Ca-Chelex resin (c. 100 mg) was introduced into 10 mL of filtered (< 0.2 µm)
 172 solution from both spiked and un-spiked soil suspensions. After equilibration for 2 hours, the resin was
 173 rinsed with MilliQ water three times to remove colloidal particles. Metals were then eluted from the
 174 resin with 0.5 M HNO₃ and the measured isotopic ratio used to calculate the labile pool (M_{Ef}; mg kg⁻¹).
 175 Results were compared with M_E measured directly on the filtered solution phase to test for the presence
 176 of non-labile SCP-metal.

177 *Comparison with radio-labile metal fraction measured in October 1999*

178 A comparison was made between values of Cd_E and Zn_E measured in this study in August and
179 September 2011, and the ‘radio-labile’ fraction (M_E^*) measured by Tye et al. (2003) on the same soils
180 in October 1999 - shortly after collection of the Urban soils but following 818 d incubation at 80% field
181 capacity in the case of the MA soils. The objective was to investigate possible further aging of Cd and
182 Zn in MA and Urban soils following 12 years of soil storage under air dry conditions. In the study of
183 Tye et al., the radio-isotopes ^{109}Cd and ^{65}Zn were used to determine Cd_E^* and Zn_E^* .

184 **2.4 Analysis of soil solution**

185 Elemental concentrations of dissolved major (Al, Ca, K, Mg and Na) and trace (Cd, Cu, Ni, Pb and Zn)
186 cations were measured in 0.01 M $Ca(NO_3)_2$ suspensions with 1 g soil in 30 mL solution using ICP-MS,
187 as described in Section 2.2. Dissolved organic carbon (DOC) and inorganic carbon (DIC) were
188 determined in the suspensions using a Shimadzu TOC-Vcp analyser. For modelling purposes, an
189 estimate of FA concentration in solution was made assuming that dissolved organic matter (DOM)
190 contains 50% C and that 65% of DOM consists of active FA (Buekers et al., 2008b; Cheng et al., 2005).

191 **2.5 Describing lability ($\%M_E$) as a function of soil properties**

192 Two types of empirical model for predicting $\%M_E$ from measured soil properties were assessed. The
193 first was a multiple linear regression model where the simplicity of the equation allows inclusion of a
194 large number of variables. Values of $\%M_E$ were correlated with a range of soil characteristics including
195 pH, %SOC, %Clay, Al, Fe and Mn oxide contents ($mg\ kg^{-1}$) and total Cd, Cu, Ni, Pb, Zn concentration
196 (M_{total} ; $mg\ kg^{-1}$). The significance of each variable was determined (Minitab vs 16.2.2) and only those
197 that were significant ($p < 0.05$) in predicting $\%M_E$ were included in the model (**Eq. 3**). The constants
198 were optimized using the *Solver* function in Microsoft Excel.

$$199 \quad \%M_E = k_0 + k_1 (pH) + k_2 (\%SOC) + k_3 (FeOx) + k_4 (MnOx) + k_5 (AlOx) + k_6 (\%Clay) + k_7 (M_{total}) \quad (3)$$

200 The second model was a logistic (sigmoid) equation based on the assumption that pH is likely to be the
201 primary determinant of $\%M_E$ (**Eq. 4**). A similar function has been shown to describe trace metal
202 *adsorption* on soil binding phases (Sinitzyn et al., 2000; Lamy et al., 1993). Metal lability was therefore
203 predicted assuming that $\%M_E$ was controlled only by pH and that the pH at which 50% of the metal
204 was labile (pH_{50}) was metal specific (**Eq. 4**).

$$205 \quad \%M_E = \frac{100}{1 + \exp[k_M(pH - pH_{50})]} \quad (4)$$

206 In **Eq. 4**, the ‘spreading factor’ (k_M) controls the slope of the model trend across the pH range and is
207 probably unique to a particular soil-metal combination. Therefore, an attempt was made to refine **Eq.**
208 **4** by making k_M a function of other soil characteristics (S) describing the role of likely metal adsorbents
209 (e.g. %SOC, metal oxide concentration and clay content); a power function (n) was added because it
210 achieved a better fit to the data in practice (**Eq. 5**).

211
$$\%M_E = \frac{100}{1 + \exp[k_M S^n (pH - pH_{50})]} \quad (5)$$

212 A further simplification was to combine the measured oxide phases into a single variable, allowing for
213 differences in the molecular weight for Al₂O₃, Fe₂O₃·H₂O and MnO₂, resulting in three variables
214 (%SOC, mineral (hydr)oxides and clay). Only one of the three variables was assumed to control the
215 spread of %M_E values with pH (**Eq. 5**) for each metal. The constants in **Equations 4** and **5** were
216 optimized, using the *Solver* function in Microsoft Excel, to assess the performance of each model.

217 **2.6 Predicting trace metal solubility and speciation by WHAM-VII**

218 The geochemical speciation model WHAM-VII was used to predict Cd, Cu, Ni, Pb and Zn
219 concentration in the solution phase of soil suspensions. Measured values of M_E were used as inputs to
220 WHAM, representing the total reactive trace metal fraction in the soil suspensions. The modelled metal
221 concentration in solution was compared with measured values to assess the model performance.
222 Speciation in solution and fractionation in the soil solid phase were derived from the model output.
223 Model parameters and variables are listed in **Appendix 1**.

224 3. RESULTS

225 3.1 *Soil characteristics*

226 Full details of soil properties for the MA and Urban soils are provided as supplementary material
227 (Appendices 2&3). Soil pH values covered a wide range, from < 4 to ~ 8; the Urban soils were slightly
228 more alkaline with 60% of pH values > 6.0. All the soils can be categorized as mineral soils (%SOC <
229 20%) with two possible exceptions; Urban soils with 20.5% and 25.1% SOC, one sampled in a public
230 park and the other near a railway line, both had evidence of coal in the soil. Urban soils from brownfield
231 sites typically had the lowest %SOC (Appendix 2). Iron oxide content (FeOx) in both sets covered a
232 wide range of values (5.4 - 43 g kg⁻¹); concentrations of Mn oxides (MnOx) were much lower than
233 FeOx (0.16 – 3.01 g kg⁻¹), but the two variables were strongly correlated ($p < 0.01$). Iron oxides strongly
234 adsorb trace metals at neutral and high pH values (Tack, 2010) whereas Mn oxides are more important
235 at lower pH values due to their lower pzc (Dong et al., 2003; Trivedi and Axe, 2001). For the MA
236 soils, uniformly amended with five trace metals, there was a relatively small variation in total metal
237 concentration resulting from native soil metal content (Tye et al., 2003; Tye et al., 2004). Total metal
238 concentrations in the Urban soils covered a much wider range as a consequence of historical
239 contamination. Some individual metal concentrations in Urban soils were strongly correlated implying
240 contamination from the same source (p -values < 0.05). Copper, Ni, Pb and Zn concentrations were
241 positively, but weakly, correlated with %SOC ($r_{Cu}=0.36$, $r_{Ni}=0.40$, $r_{Pb}=0.45$, $r_{Zn}=0.43$), FeOx ($r_{Cu}=0.47$,
242 $r_{Ni}=0.41$, $r_{Pb}=0.37$, $r_{Zn}=0.43$) and MnOx ($r_{Cu}=0.48$, $r_{Ni}=0.39$, $r_{Pb}=0.32$, $r_{Zn}=0.38$) possibly as a result of
243 their accumulation in soils with strong binding phases (Rieuwerts et al., 2006; Zimdahl and Skogerboe,
244 1977). Cadmium concentration was less affected by soil properties, only showing a very weak
245 correlation with AlOx ($r_{Cd}=0.34$).

246

247 3.2 *Measured metal lability in soils*

248 Values of %M_E for Cd, Cu, Ni, Pb and Zn are shown in **Fig. 1**. For Urban soils the average %M_E values
249 were 47.2% (Cd), 20.5% (Cu), 6.28% (Ni), 21.1% (Pb) and 18.1% (Zn) emphasising the need to
250 consider metal lability (i.e. M_E, mg kg⁻¹), rather than just total soil metal content, when assessing risk
251 and mobility in brownfield sites. Values of metal lability in the MA soils were significantly greater
252 than in the Urban soils with average %M_E values of 74.4% (Cd), 48.7% (Cu), 36.2% (Ni), 54.1% (Pb)
253 and 41.5% (Zn) despite three years incubation of MA soils at 80% field capacity and a further 12 years
254 of storage under air dry conditions. In both sets of soils, the relative lability of the five metals followed
255 the same sequence (Cd > Pb ≥ Cu > Zn > Ni).

256 The presence of a non-labile fraction of metal in suspended colloidal particles (SCP-metal) in the
257 submicron filtered (< 0.22 μm) supernatant solutions from the soil suspensions used to measure M_E
258 values was investigated by comparing M_E and M_{Ef} (**Appendix 3**). For most of the soils, SCP-metal had
259 only a very small effect on measured E-values. There was a strong correlation between %M_E and %M_{Ef}
260 and an average difference of less than 2% for all five metals; a significant difference was only observed

261 for Cu in the soils investigated. The ratio of $Cu_E : Cu_{EF}$ against soil pH and $\%Cu_E$ (**Fig. 2a & 2b**) clearly
262 suggests the presence of SCP-Cu, despite filtration to $< 0.22 \mu m$, especially at low levels of $\%M_E$ and
263 high pH values in the Urban soils.

264 **3.3. Predicting metal lability from soil properties**

265 The effects of soil properties on values of $\%M_E$ were described in two ways: a multiple-regression
266 model, which has the advantage of being able to include many variables, and a simple logistic model
267 with soil pH as the primary determining factor.

268 In the current study, seven variables were available to predict values of $\%M_E$ from **Eq. 3**. Metal lability
269 in the Urban soils is likely to have been affected by factors other than soil properties, especially metal
270 source characteristics. Therefore, **Eq. 3** was parameterized using data from the MA soils only in which
271 the added metal was from a single, initially dissolved, source. The goodness of fitting was evaluated
272 from the values of RSD and correlation co-efficient (r). A good level of prediction was achieved for Cd
273 ($r=0.92$, $RSD=6.3$), Ni ($r=0.97$, $RSD=5.85$) and Zn ($r=0.95$, $RSD=7.7$), but Cu and Pb were less
274 successfully modelled, with correlation co-efficient equals to 0.83 and 0.85 respectively. Soil pH was
275 negatively correlated with $\%M_E$ for all five metals and accounted for the largest proportion of the total
276 variance in $\%M_E$ in the MA soils: 63.2%, 25.5%, 73.1%, 53.3% and 66.1%, for Cd, Cu, Ni, Pb and Zn
277 respectively. The optimized constants, RSD values and correlation co-efficients (r) are summarized in
278 **Appendix 4**.

279 Although linear regression modelling can provide reasonable predictions of metal lability where $\%M_E$
280 is largely a function of soil characteristics and a single contaminant source predominates, as in the MA
281 soils, the application of this model is limited to the range of data used to parameterise the model.
282 Extending 'prediction' of lability outside this range can result in physically impossible outcomes in
283 which modelled values of $\%M_E$ may be negative, or $> 100\%$. By contrast, a sigmoidal model (**Eq. 4**)
284 offers more realistic boundaries to model outcomes ($\%M_E = 0 \sim 100\%$). The sequence of optimized
285 pH_{50} values was $Cd > Pb > Cu > Zn > Ni$, and covered nearly three pH units, in agreement with the
286 expected order of metal lability. The exponential factor k_M is related to the range of pH values over
287 which the major change in $\%M_E$ occurs. Inclusion of each of the adsorption phases (OM, oxides, and
288 clay) was then used to try and refine prediction of $\%M_E$ according to **Eq. 5**. For Cd, Ni and Zn, the best
289 prediction, lowest RSD and highest value of r , was achieved by including total oxide content within **Eq.**
290 **5** (S value) to control the spread of predicted $\%M_E$ values as a function of pH. For Cu and Pb, including
291 total oxide content also improved prediction of $\%M_E$, but the lowest RSD was obtained by including
292 clay and organic matter content respectively. Copper produced the lowest k_M value (0.16) and so only
293 gradually undergoes transition from labile to a fixed state over a relatively large range of pH values,
294 whereas Ni and Zn were labile over a more restricted range of pH values with k_M values equal to 0.76
295 and 0.72 respectively. The optimized values of pH_{50} and the exponential constant k_M in **Eq. 4 & 5**,
296 together with the results of modelling for the MA soils are shown in **Appendix 5**.

3.4. *Metal lability in MA and Urban soils solely as a function of soil pH*

Measured values of %M_E for Cd, Cu, Ni, Pb and Zn in MA and Urban soils, as a function of pH value, are shown in **Fig. 3** with model lines derived from **Eq. 4**. In the MA soils, for all five metals, there was no obvious bias in model prediction across the pH range. Measured values of Cu lability were only weakly correlated with pH. Although Cd and Pb also showed a restricted range of %M_E values, lability exceeded 90% and 80%, respectively, below pH 4.0. Zinc and Ni in the MA soils both showed substantially greater variation in %M_E with pH compared to the other three metals. Only small and non-significant differences between predicted values of %M_E were achieved by substituting **Eq. 5** for **Eq. 4** ($p > 0.05$) which implies no advantage in considering an effect of geocolloidal adsorption phase in the sigmoidal equation. The values of pH₅₀ optimized using **Eq. 4** were very similar to those for **Eq. 5** and followed the observed sequence of relative metal lability in soils (**Appendix 5**). The measured values for the Urban soils are shown for comparison with the MA soils in **Fig. 3**. Soil pH affected metal lability in the Urban soils with a trend qualitatively similar to that of the MA soils but %M_E values were greatly over-predicted by the model (**Eq. 4** parameterised using the MA soils) in all cases.

Possible source effects were investigated by calculating the deviation from the model line as a proportion (%) of the modelled E-value (% Δ M_E); the model being parameterized solely from the MA soils for each element. No correlation between % Δ M_E and pH or %C was observed with the exception of Pb where a trend with pH was apparent ($r = 0.602$) suggesting either a pH effect on the *source* of Pb or a continuing effect of soil-metal contact time (greater for the Urban soils). Thus, overestimation of %M_E values for Pb was greater for soils with high pH and low metal lability.

3.5. *Changes in Cd and Zn lability in air dried soils during storage*

For the MA soils, a paired t-test showed that the difference between M_E and M_E^{*} measured using radioisotopes by Tye et al. (2003) was significant for Zn ($p = 0.007$), but not for Cd ($p = 0.416$). However, for the Urban soils, there was a significant difference for both Zn and Cd ($p < 0.001$) with, generally, %M_E^{*} > %M_E (**Fig. 4a**). It is notable, for example, that the difference between M_E and M_E^{*} was more pronounced in high pH soils than in acidic soils (**Fig. 4b**). However, only a very small difference between M_E and M_E^{*} was observed in MA soils; the average ratio M_E : M_E^{*} was 0.93 and 1.00 for Zn and Cd respectively. In contrast, for the Urban soils the ratios were 0.71 and 0.69 for Zn and Cd.

3.6. *WHAM-VII prediction of metal solubility and fractionation*

The ability of the geochemical speciation model, WHAM-VII, to predict Cd, Cu, Ni, Pb and Zn concentration in solution is shown in **Fig. 5** as modelled against measured solubility on a $-\log_{10}$ scale (pM_{soln}). Values of M_E were input to the model to represent the reactive metal pool in the soil suspensions (**Appendix 1**). Overall WHAM-VII predicted trace metal solubility reasonably well for both sets of soils. The values of RSD were less than 1 (pM_{soln} unit) for all five metals although the

332 average absolute bias ($\Delta p(M_{\text{soln}})$) differed between metals. Summary of model outcomes comparing the
333 measured and the predicted are provided in the Appendix 6.

334 Predictions of Cu, Ni, Cd and Zn solubility were only slightly better for MA soils than for the Urban
335 soils but the difference for Pb was greater: r values for Pb were 0.96 and 0.78 for MA and Urban soils
336 respectively. Among the five metals, the model gave the best prediction for Cd and Ni with relatively
337 low scatter around the 1:1 line (RSD = 0.51 and 0.63 respectively) and a high correlation coefficient (r
338 = 0.94 for both metals). The high RSD value for Zn (0.83) occurred because the model substantially
339 overestimated the solution concentration for several Urban soils with high pH values (6.93 to 8.08) and
340 very low Zn concentrations in solution. Prediction of Cu solubility was reasonably good (RSD = 0.45;
341 $r = 0.74$) but with some Urban soil outliers. Lead solubility was most poorly predicted by WHAM-VII
342 (RSD=0.64; $r=0.85$). However, splitting the Pb dataset between MA and Urban soils, it was clear that,
343 although there was less average bias compared to the other metals, the poor correlation coefficient and
344 large RSD value was due to the Urban soils (RSD = 0.73, $r = 0.78$, $\Delta pPb_{\text{soln}} = -0.08$), whereas solubility
345 for the MA soils was more accurately predicted although with very slightly greater bias (RSD = 0.35, r
346 = 0.96, $\Delta pPb_{\text{soln}} = 0.11$).

347 Trace metal fractionation in the solid phase is provided by WHAM-VII as an output. Therefore, metal
348 adsorption on different binding phases was investigated by interrogation of the WHAM-VII output data
349 to determine whether particularly large deviations between measured and predicted metal solubility
350 were associated with predominant sorption on particular binding phases. Average fractionation was
351 modelled using WHAM-VII and includes six particulate geocolloidal fractions and a single pool for the
352 solution phase, including 'colloidal' (dissolved) fulvic acid. **Figure 6** illustrates the average proportions
353 of *labile* Cd, Cu, Ni, Pb and Zn predicted to be held in different soil phases alongside with changes in
354 metal lability as a function of soil pH for both MA and Urban soils, as a combined dataset. For all five
355 metals, **Figure 6** suggests that the relative importance of Fe-oxides for metal binding increases with pH,
356 whilst that of organic matter (HA and FA) decreases. The WHAM model predicted that, on average,
357 96% of the Pb was adsorbed on Fe and Mn oxides for the MA and Urban soils; Mn oxides were more
358 important below pH 6.5. By contrast, organic matter was most important for Cu across the pH range
359 studied. Non-specific adsorption of Cd, Ni and Zn on clay was only significant in soils with very low
360 pH values (pH 3.5 – 4.5) and low organic matter contents - less than 2.3%, 2.4% and 2.1% respectively.

361 Various factors may affect WHAM model performance in predicting metal solubility including soil pH
362 and solid binding phase. The influence of soil pH value on model performance was statistically
363 significant for Cd, Cu, Ni and Zn ($p < 0.01$), but not for Pb. Overestimation of metal solubility (log
364 scale) increased with soil pH to give a positive correlation coefficient between ΔpM_{soln} (i.e. bias between
365 the predicted and measured solubility by WHAM on $-\log$ scale) and pH. For Cd, Ni and Zn, the bias
366 (ΔpM_{soln}) observed seemed to be mainly associated with the (modelled) proportion of labile metal bound
367 to Fe oxides—especially for Cd and Zn in the high pH range (positive correlation coefficient). In the

368 case of Cu, bias was affected by Cu binding to particulate Mn oxides, and HA and colloidal (solution
369 phase) FA. There was less over-prediction of solubility with increase in the proportion of Cu bound
370 with HA and greater over-prediction with binding to colloidal FA-Cu. Prediction bias for Pb was
371 relatively unaffected by soil pH or by the proportion bound to either Fe or Mn oxides; the range of bias
372 was greater for the Urban soils. Correlation (r) between ΔpM_{soln} and soil pH or percentage binding with
373 an important particulate phase (FeOx, MnOx, AlOx, HA) or colloidal (dissolved) phase (FA) are
374 presented in Appendix 7.

375

376 4. DISCUSSION

377 4.1 *The effect of soil properties and metal source on metal lability*

378 Greater metal lability in the MA soils (**Fig. 1**) may partly reflect different soil-metal contact times for
379 the two soil datasets, but it seems very likely that the characteristics of the original metal source are
380 also responsible for lowering the lability in Urban soils. A similar conclusion regarding Cd lability in
381 field contaminated soils was also made by Degryse et al. (2004) comparing radio-labile Cd in soils
382 sampled adjacent to a smelter and ‘metal salt incubated soils’ but with a much shorter period of
383 incubation.

384 The relative lability of the five metals in both MA and Urban soils followed the sequence $Cd > Pb \geq$
385 $Cu > Zn > Ni$ which agrees with the observations of Gabler et al., (2007) who measured the lability of
386 these five metals on 115 unpolluted soil samples using a stable isotope dilution approach. In the MA
387 soils, where metal ions were originally added in solution, the difference in lability of the five metals
388 only partly reflects their expected rates of fixation into soil constituents, based on a negative correlation
389 with ionic radius, i.e. $Ni \geq Cu > Zn > Cd \sim Pb$ (Degryse et al., 2009; Degryse et al., 2007). The relatively
390 larger proportion of Zn and Ni fixed may have been due to substitution for Fe in oxyhydroxides
391 (Buekers et al., 2008a; Manceau et al., 2000), a mechanism which is less likely for larger ions such as
392 Cd and Pb (Buekers et al., 2008a; Xu et al., 2006). However, the lower lability of Pb compared to Cd
393 may be due to Pb precipitation as pyromorphite in phosphate-rich soils (Dermatas et al., 2008). Copper
394 is predominantly bound with organic matter which may result in a slightly higher lability compared to
395 Zn sorbed *within* Fe oxides.

396 For Ni and Zn, a smaller range of lability was seen in the Urban soils than in the MA soils. This may
397 be counter to expectation because the Urban soils had a larger range of metal contaminant sources and
398 the *range* of soil pH values (a major determinant of $\%M_E$) in the MA and Urban soils were broadly
399 similar (**Appendix 2**). However, the lower lability of metal sources in the Urban soils also probably
400 acts to limit the range of $\%M_E$ values in comparison with the MA soils. A restricted range of low $\%M_E$
401 values have also been reported for Pb in calcareous minespoils soils (Degryse et al., 2004; Marzouk et
402 al., 2013a) and for Cd and Zn in soils contaminated with smelter wastes (Degryse et al., 2004). However,
403 the greater lability of Cd in the Urban soils, relative to other metals, does not necessarily indicate that

404 the original source of Cd was more soluble. It has been shown that Cd and Zn added to soil in identical
405 (isomorphically substituted) forms (e.g. sphalerite) nevertheless end up with quite different labilities
406 following prolonged exposure to soil processes (Marzouk et al., 2013a; Degryse et al., 2004).

407 **4.2 Prediction of metal lability**

408 Poor prediction of %M_E for Cu and Pb compared to Cd, Ni and Zn (**Appendix 4**) may arise from several
409 factors. It is widely recognised that adsorption on humus dominates Cu dynamics in soils (Weng et al.,
410 2001) but no significant correlation was found between Cu lability and %SOC in this study ($p > 0.05$).
411 Another possible explanation is a failure to include factors which might promote strong Cu binding
412 phases in the model, such as sulphide content (Du Laing et al., 2009). In some soils Pb is likely to
413 precipitate in non-labile mineral forms such as chloropyromorphite (Pb₅(PO₄)₃Cl) (Lang and
414 Kaupenjohann, 2003); fractionation of Pb in soils is generally less well described by current
415 geochemical models (Gustafsson et al., 2011).

416 The importance of pH as a predictor of lability (**Appendix 4**) is in agreement with previous studies
417 (Rieuwerts et al., 2006; Marzouk et al., 2013b). Stronger adsorption of metals is certainly expected with
418 increasing pH, partly due to the increase in negative charge on all adsorption surfaces. Metal *fixation* is
419 not necessarily linked directly to strength of adsorption, but it seems reasonable to assume that factors
420 that increase adsorption strength will also reduce isotopic exchangeability. Other processes may also
421 explain the influence of pH on lability, including preferential adsorption of metal hydroxide complexes
422 (Basta and Tabatabai, 1992) and precipitation as carbonate phases, (e.g. Gambrell, 1994; Charlatchka
423 and Cambier, 2000). In calcareous soils, diffusion into carbonate minerals (Hamon et al., 2002; Collins
424 et al., 2003; Buekers et al., 2007; Ahmed et al., 2008), or surface precipitation reactions (Ma et al.,
425 2006b; Nazif et al., 2015) are important. The significance of individual soil properties in
426 predicting %M_E was metal-specific; a positive coefficient (**Eq. 3**) may suggest that the adsorbent holds
427 labile metal and a negative coefficient may indicate a source of metal fixation. Thus the addition of
428 FeOx improved the prediction for Ni and Zn possibly suggesting that an important mechanism for metal
429 fixation is diffusion into Fe oxide micropores (Jacquat et al., 2009; Manceau et al., 2000; Degryse et
430 al., 2011). Although MnOx was correlated with the lability of all five metals (**Appendix 4**), it explained
431 $\leq 0.4\%$ of total variance in predicting %M_E for Cd, Ni and Zn. For Cu and Pb, MnOx was more
432 important, accounting for 4.8 and 8.2% of the total variance in %M_E with a negative coefficient, which
433 is in agreement with previous studies (Bonten et al., 2008; Weng et al., 2001). The contribution from
434 clay content was extremely limited; only a very small proportion of 'isotopically labile' trace metal ions
435 are normally exchangeable with a neutral alkali-earth salt (Nakhone and Young, 1993). The correlation
436 with clay content may reflect a general association with soil mineral geocolloid content, rather than
437 implying that Zn and Ni are fixed within alumino-silicate clay minerals. Nevertheless, specific
438 adsorption of Zn within hydroxyl-interlayered clays in acidic soils has been demonstrated by Degryse
439 et al. (2011). Finally, there was a negative correlation between total Cd, Ni and Zn and content and

440 values of %M_E, probably because the larger content of native metal in the Urban soils (especially Zn)
441 was less labile than the (fixed amount of) metal ions added as soluble salts to the MA soils.

442 The logistic model performance was generally slightly poorer than the fit achieved with multiple linear
443 regression (**Appendix 4 and 5**). However, **Eq. 4** has parameters (pH₅₀; k_M) that are more clearly related
444 to the mechanisms that control trace metal lability and provides extrapolative predictions that remain
445 realistic. Therefore, the simple logistic equation, expressing %M_E solely as a function of pH, is perhaps
446 a more robust model for predicting metal lability solely and more useful than regression coefficients for
447 comparative purposes.

448 Over-prediction of %M_E values in the Urban soils compared to the MA soils probably reflects the
449 characteristics of the contaminant source on metal lability. This conclusion is further supported in **Fig.**
450 **3** by the greater scatter of %M_E values for the Urban soils seen for Cu and Cd and perhaps also the
451 flatter trend with pH seen for Ni and Zn in Urban soils suggesting a primary mineral source less affected
452 by pH-dependent adsorption strength. In the Urban soils set, more than half of the high pH soils (> 6.5)
453 were associated with old industrial sites, i.e. brownfield, wasteland, etc. (Appendix 2), where metals
454 probably entered the soils in a relatively non-soluble form. Secondary formation of poorly soluble
455 minerals in calcareous soils (Degryse, et al., 2009) or Pb minerals (e.g. cerussite or chloropyromorphite)
456 would also contribute to the trend seen. For example, the average measured lability of Pb in two
457 phosphate-rich sewage farm soils (NG14 & NG15, 13.8%) was much less than that predicted by the
458 MA-parameterized model (50.0%) suggesting precipitation of Pb phosphate minerals either in the soil
459 or during the processing of the sewage sludge. However, it was difficult to identify any specific effects
460 of historical or current land use on lability as, for example, soils from 'brownfield sites' produced values
461 of %M_E for Cu ranging from 5.6% – 30.5% (NG19 and NG18, Appendix 2).

462 No effect of pH on % Δ M_E was identified for Ni or Zn. A potential explanation is that Ni in these soils
463 may be mostly attributable to parent material; this is supported by the low total Ni concentrations found
464 (mean = 38.5 mg kg⁻¹; SD = 18.4 mg kg⁻¹). Only two soils had substantially higher Ni concentrations
465 (**Fig. 3**). These were both from a sewage farm (NG14 and NG15) and had the highest values of %Ni_E
466 (34.4% and 42.9%, respectively), suggesting that Ni lability in the sludge was high and that the soil-
467 contaminant interaction was closer to the behaviour seen in the MA soils. It has been suggested
468 previously that metal lability can be more dependent on the characteristics of the sludge than properties
469 of the soil (Stacey et al., 2001). For example immobilization of soft acids such as silver, by soft bases
470 such as sulphide has been recognized in biosolids (Donner et al., 2015; Donner et al., 2013). This
471 suggests that Ni, as an intermediate metal cation, will be more strongly held by carboxyl groups in the
472 organic matter of the sludge and remain labile. In contrast to Ni, total Zn concentrations in the Urban
473 soils (mean = 283 mg kg⁻¹; SD = 178 mg kg⁻¹) were generally higher than in most soils in England and
474 Wales in which Zn is typically <100 mg kg⁻¹ unless contaminated by minespoil (Rawlins et al., 2012).
475 Therefore it can be assumed that the Urban soils received Zn from sources other than parent material.

476 It is difficult to summarize the effect of land use on metal lability for the whole dataset because of the
477 complex range of Zn sources. For example, from field notes, metals in soil WV20 were probably
478 associated with canal dredgings whereas soil WV25 was contaminated from its location in an industrial
479 estate and proximity to a railway - but both soils had similar values of %Zn_E (27.7% and 20.6%
480 respectively). There was only one sample where Zn lability was, unexpectedly, underestimated by the
481 MA-parameterized model and fell slightly outside of the RSD range: soil WV3 was a slightly acidic
482 woodland soil (pH = 6.1) with very high DOC concentrations (180 mg L⁻¹ in 0.01 M CaCl₂, 1g: 30 mL).

483 **4.3 Aging of Cd and Zn in air dried soils during storage**

484 The difference between values of M_E measured in the current study and M_E* measured by Tye et al.
485 (2003) for Cd and Zn may be a consequence of processes occurring within the soils or it may be the
486 result of analytical artefacts in either of the two methods (**Fig. 4**). Only a limited number of studies have
487 compared the measurement of metal lability using both radio-isotopes and stable isotopes. Sterckeman
488 et al. (2009) compared Cd lability measured using ¹¹¹Cd (stable; M_E) and ¹⁰⁹Cd (radioactive; M_E*) and
489 found that the results were equivalent but that M_E data were more repeatable. Considering the range of
490 properties of the MA soils, continuing fixation of Zn may have occurred in some soils. Even in air-dried
491 soils, particles may have thin films of surface hydration which could mean that the soil remains
492 sufficiently chemically reactive to allow solid phase matrix- and surface-diffusion processes.

493 The greater difference between M_E and M_E* for the Urban soils was surprising as there was no
494 expectation of measureable metal fixation during the 12 years of air dry storage prior to measurement
495 of M_E in August and September 2011 whereas further slow fixation in the MA soils was expected. This
496 result may indicate a methodological difference. Values of M_E* were determined using flame-AAS
497 and graphite furnace-AAS measurement of Cd and Zn combined with radio-assay of ¹⁰⁹Cd and ⁶⁵Zn in
498 solution following centrifugation of soil suspensions at 2200 g. Values of M_E were determined solely
499 by ICP-MS following additional filtration to < 0.22 μm. Thus, the (large) values of M_E* measured in
500 1999 may have been more susceptible to the influence of non-labile metal in suspended submicron
501 particles (Lombi et al., 2003) - an effect which is enhanced at (i) higher pH values, (ii) lower soluble
502 metal concentrations and (iii) lower values of %M_E - which are all characteristics of the Urban soils.

503 **4.4 Effect of non-labile soil colloidal particles on measured E-value**

504 A strong correlation between %M_E and %M_{E_r} was expected because as metal lability increases there is
505 less scope for a substantial effect from non-labile SCP-metal as M_{E_r} gradually approaches the value of
506 M_E at 100% lability. The increase in Cu_E/Cu_{E_r} with pH (**Fig. 2b**) is in agreement with previous
507 explanations of more mobile geocolloidal particles in the soil solution at higher pH values (Lombi et
508 al., 2003; Nolan et al., 2009; Marzouk et al., 2013b). The presence of non-labile soluble Cu has also
509 been shown to arise from strong adsorption of Cu on humic acid (Mao et al., 2015) whereas other trace
510 metal ions (Cd, Ni, Pb and Zn) are more likely to be associated with colloidal Fe, Al and Mn oxides
511 (Lombi et al., 2003; Ma et al., 2006a; Nolan et al., 2009). However, in this work no significant

512 correlation ($p > 0.05$) was observed between the ratio of $M_E:M_{E_f}$ and solution concentration of Fe, Al,
513 Mn or DOC measured in 0.01 M $\text{Ca}(\text{NO}_3)_2$ (solid: solution ratio 1 g : 30 mL).

514 **4.5 Prediction of metal solubility and fractionation with WHAM-VII**

515 *Metal binding*

516 For all five metals the relative importance of Fe-oxides for metal binding appeared to increase with
517 increasing pH whilst that of organic matter (HA and FA) decreased (**Fig. 6**). The pH-dependency of
518 metal adsorption to Fe oxide is stronger than that of organic matter (Weng et al., 2004) and Fe oxide
519 appeared to control metal binding at high pH ($> \text{pH } 7$), except in the case of Cu where organic matter
520 was most important. Most of the Cu ($> 91.0\%$) and Pb ($> 92.3\%$) were absorbed by the soil across the
521 pH range, even at low pH values, although there were substantial differences in their affinity for
522 particular binding phases.

523 *Errors associated with modelling*

524 Errors in prediction of metal solubility may arise for reasons originating in both modelling and
525 measurement. Model shortcomings may include poor parameterisation of the 'pure' geocolloidal metal
526 binding parameters and failure to include all binding phases. The default constants in WHAM were
527 originally parameterized on single geocolloidal systems and the most comprehensive datasets used in
528 the sub-model employed (Model VII) were from studies of metal binding by purified humic and fulvic
529 acids. Therefore it is likely that soils in which humus is the dominant adsorption surface are likely to
530 perform better than those with complex assemblages of organic and mineral geocolloids. As suggested
531 by Smith et al. (2004) the properties of the cation binding sites of humic substances in peat appear very
532 similar to those of isolated humic substances. It has also been shown in other studies that prediction of
533 the trace metal solubility with multi-surface geochemical models is more successful when solid \rightleftharpoons
534 solution partitioning is controlled mainly by soil organic matter (Weng et al., 2002; Cances et al., 2003).

535 In contrast to Model VII for HA and FA, the surface complexation model for describing metal speciation
536 on mineral oxides may be less rigorous in (i) combining all soil oxide adsorbents into just three types
537 (Al, Mn and Fe oxides) and (ii) using a single parameter to describe heterogeneity for all metals (Lofts
538 and Tipping, 1998) and oxides (default setting). Such simplifications are reasonable to avoid the need
539 for a large parameter database limiting the applicability of the model. However, it may also be the
540 reason for greater deviation from measured values in predicting solubility in high pH soils in which
541 oxides are the dominant metal binding phases. Soils will have a range of oxide minerals, which vary in
542 surface charge characteristics, surface morphology/area, crystallinity and degree of surface
543 contamination with adsorbed anions and humus acids. All of these factors together will generate a
544 range of adsorption strengths for metal cations. As pH rises, a greater range of metal oxides contribute
545 to cation binding and so the *diversity* of oxide surfaces involved in metal adsorption will increase.
546 Therefore, if a speciation model generates error in predicting metal binding on oxides surfaces, the
547 effect is likely to be more significant in high pH soils as there is an accumulation of error contributed

548 by each oxide phase. In addition, there are other binding phases in soils which may actively adsorb
549 metal cations especially in high pH soils. For example, calcite (CaCO_3) and hydroxyapatite
550 ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), which are only likely to be present in soils with high pH (> 7.0 and > 6.0 respectively),
551 can adsorb metal cations by surface replacement of Ca^{2+} on mineral surface sites (Davis et al., 1987;
552 Ahmed et al., 2008; Bailey et al., 2005). The exclusion of these phases in the WHAM model may
553 contribute to the general over-prediction of solution metal concentration at high pH. Alternative
554 explanations offered within the literature include a failure to account for (i) synergistic effects
555 associated with adsorption on mixed oxide-humic surfaces (Heidmann et al., 2005; Pedrot, et al., 2009);
556 (ii) the existence of highly specific sites on Fe oxides with much greater intrinsic stability constants
557 than used in the general surface complexation model (Buekers et al., 2008b; Linde et al., 2007) or (iii)
558 formation of discrete solid phases such as chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) (Degryse et al., 2009),
559 which is likely to affect Pb dynamics in some of the Urban and sewage sludged soils.

560 *Errors associated with measurement*

561 Reasons for over-estimation and scatter in predicted solubility may lie not only with model limitations
562 but also with the measurements undertaken to provide model inputs. Using reactive trace metal
563 concentrations based on M_E values instead of ‘total’ improves the model prediction (Marzouk et al.,
564 2013b). However, poor model input data is also likely to arise from the various ‘proxies’ that are used
565 to represent geocolloidal binding phases. For example soil organic carbon is typically used to estimate
566 soil humic and fulvic acid while the Fe, Al and Mn oxide phases are rather crudely represented by
567 elemental extraction with a reducing reagent such as dithionite-citrate-bicarbonate solution. A
568 significant underestimation of measured solubility ($> \text{RSD}$) was seen for a small number of soils (e.g.
569 WV7 for Ni, Cu and Pb; WV10 for Pb, **Figure 5**). This may be a result of overestimation of some of
570 the binding phases. For example, for soil WV7, WHAM predicted 70%, 83% and 97% of binding on
571 Fe oxides for Cu, Ni and Pb, and the bias was -1.62, -0.83, and -2.25 respectively; this implies over
572 prediction of metal binding on Fe oxides. Given that generally the model algorithms *underestimate*
573 metal binding on mineral oxides, overestimation of metal binding suggests that, for these soils, the DCB
574 method extracted more Fe than was actually present in the Fe oxides phase, leading to an overestimation
575 of the Fe oxide content.

576 *Bias in prediction of metal solubility in Urban soils*

577 WHAM prediction of solubility in Urban soils generally produced a poorer correlation than that for MA
578 soils. This may be the result of slightly higher pH values in Urban soils as a consequence of the presence
579 of alkaline wastes such as cement, concrete etc. (Bridges, 1991; Rosenbaum et al., 2003). The higher
580 metal sorption capacity seen in some brownfield soils, compared to non-urban soils, is thought to
581 involve processes of both sorption and precipitation (Markiewicz-Patkowska et al., 2005; Mclean and
582 Bledsoe, 1992). Some particular examples include (i) a large bias (ΔpM) observed for Zn and Pb with
583 values of 1.7 and 1.8 respectively in soil WV21; (ii) extremely low metal solution concentrations which
584 lead to greater experimental error in some urban soils - e.g. Zn in NG13 with pH 7.0 and total Zn

585 concentration 26 mg kg⁻¹; (iii) a very high binding capacity in sewage farm soils, possibly due to
586 extremely high phosphate concentrations from the sewage sludge resulting in overestimation of Cd
587 solution concentrations in NG14 and NG15.

588 **5. CONCLUSIONS**

589 For all five metals, lability in the MA soils was significantly greater than in the Urban soils, although
590 the relative lability of the five metals followed the same sequence (Cd > Pb ≥ Cu > Zn > Ni) in both
591 sets of soils. Lower metal lability in the Urban soils may reflect longer soil-metal contact times but also
592 strongly suggests that metal source characteristics are more important. In the MA soils, a good
593 prediction of %E-value was achieved using both linear and logistic models with pH value as clearly the
594 most important soil property. Lability of Cu was least affected by soil properties. The addition of FeOx
595 improved the prediction for Ni and Zn lability, while MnOx was important for Pb at pH values < 5.5.
596 However, although the performance of the logistic model was no better than the linear one, it offers
597 more realistic boundaries to model outcomes (%M_E = 0 – 100%) and is therefore perhaps a more robust
598 model for predicting metal lability solely from soil properties and more useful than regression
599 coefficients for comparative purposes. Soil pH affected metal lability in the Urban soils in a trend
600 qualitatively similar to that of the MA soils. However, in all cases, the effect of contaminant source was
601 evident from gross over-prediction of %E-value in Urban soils using logistic models parameterized with
602 data from the MA soils. Continuing fixation of Cd and Zn may have occurred during soil storage. A
603 more pronounced difference between M_E and M_E* was observed in high pH soils than in acidic soils.
604 However, the difference between lability measured in 1999 and in the current study may also be due to
605 the influence of non-labile SCP-metal in the earlier measurement.

606 Overall WHAM-VII predicted trace metal solubility reasonably well for both sets of soils and bias was
607 observed mainly in soils with low metal solubility and relatively high soil pH values. For Cd, Ni and
608 Zn, the bias observed was primarily associated with the proportion of labile metal predicted to bind to
609 Fe oxides. In the case of Cu solubility, prediction bias was affected by Cu binding to particulate Mn
610 oxides, and HA and colloidal (dissolved) FA. Of the five metals, Pb solubility was most poorly
611 described. Solubility of all metals was predicted more accurately in the MA soils than in the Urban
612 soils. This was likely to be the result of slightly higher pH values in the Urban soils or could indicate
613 that the influence of metal source was not completely eliminated by using isotopically exchangeable
614 metal as our best estimate of the labile metal pool required as input to WHAM VII. The poorer
615 performance of WHAM-VII in predicting metal solubility in high pH soils may be the result of errors
616 in modelling, including the exclusion of potential adsorption surfaces such as CaCO₃, or simplicity of
617 the sub-model describing metal binding with mineral oxides. However there must also be considerable
618 error associated with the simplistic representation of binding phases by measurement of ‘extractable’
619 Fe and bulk soil organic carbon.

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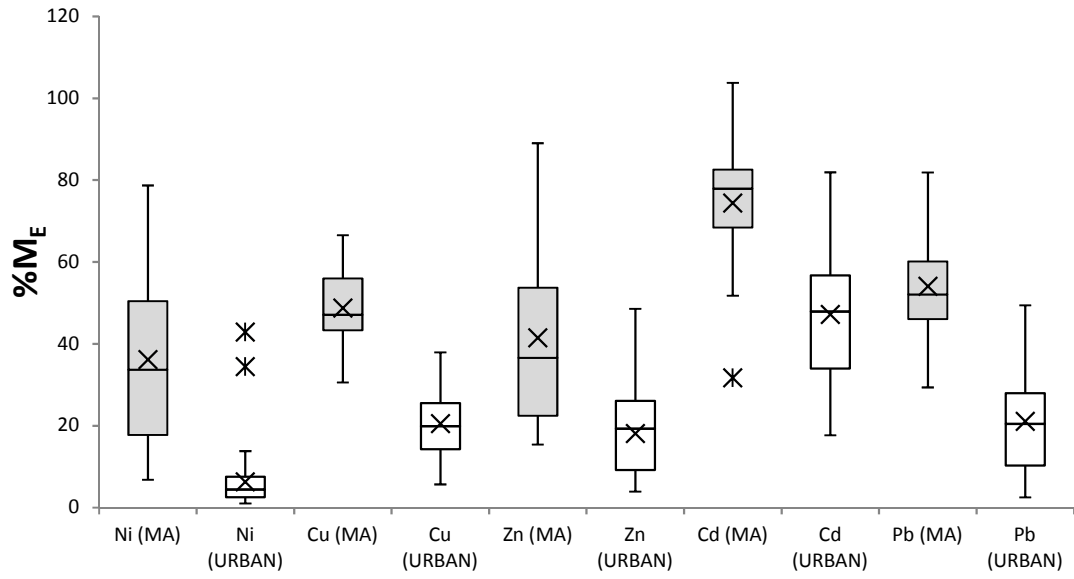


Figure 1: Box and whisker plot showing lability of Cd, Cu, Ni, Pb and Zn (% M_E) for MA soils (23) and Urban soils (50); the mean value (x) is also shown and outliers are marked as an asterisk.

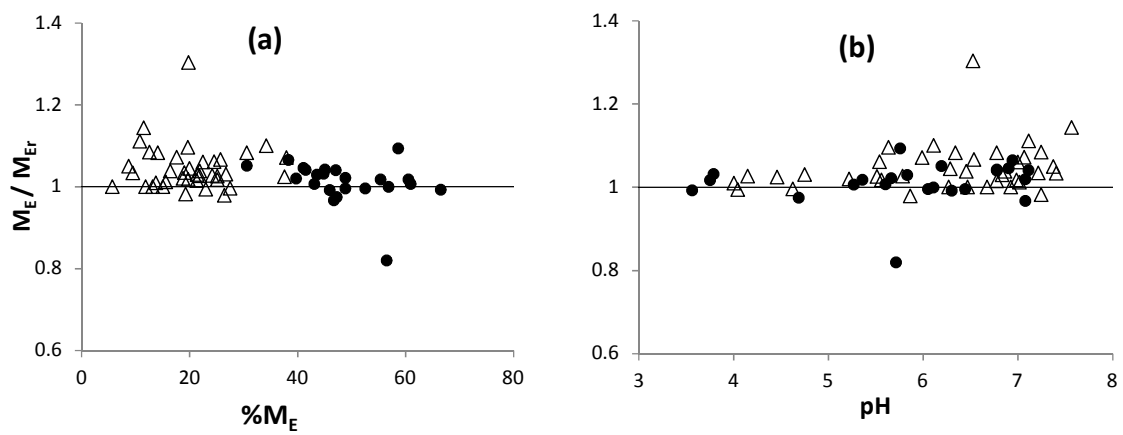


Figure 2: Ratio of $M_E : M_{Er}$ as a function of $\%M_E$ (a) and pH (b) for Cu in MA (●) and Urban (Δ) soils.

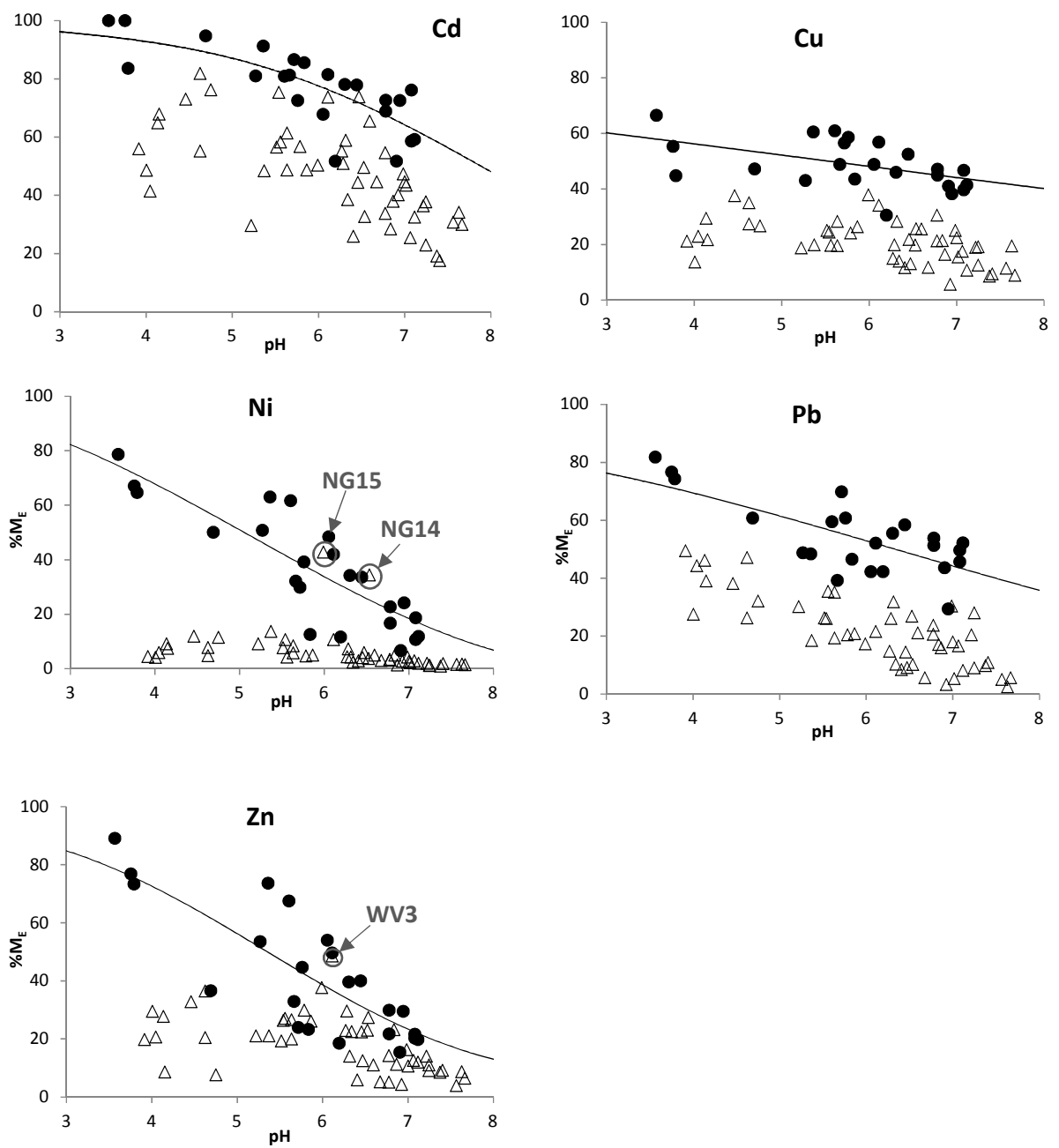


Figure 3: Measured values of %M_E (Cd, Cu, Ni, Pb and Zn) for MA (●) and Urban (Δ) soils. The solid line represents the predicted trend in %M_E from Equation 4.

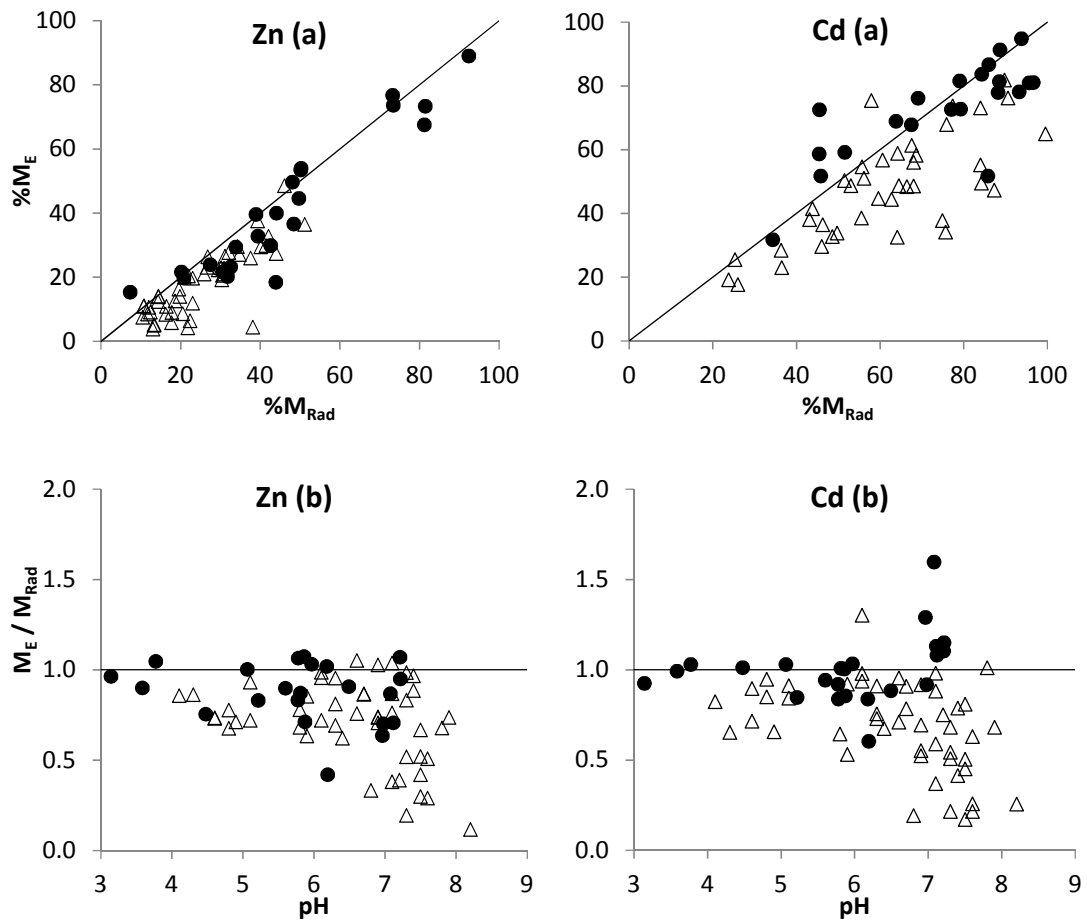


Figure 4: (a) Comparison of %M_E (this study) and %M_E* (Tye et al., 2003) for Zn and Cd in MA (●) and Urban (Δ) soils; the solid line is the 1: 1 line. (b) The ratio of M_E : M_{Rad} as a function of pH.

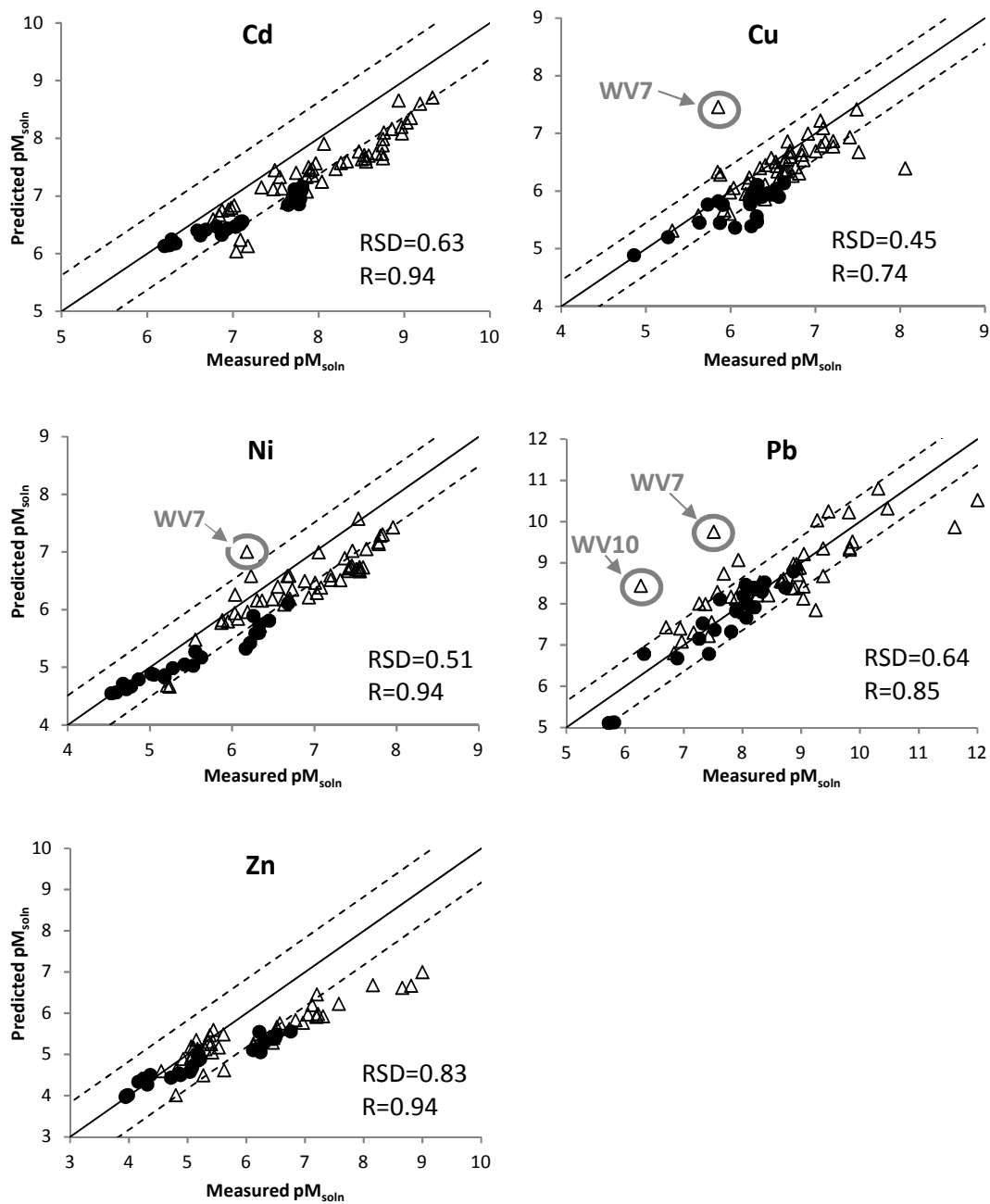


Figure 5: Solution concentrations ($pM_{soln} = -\log_{10}(M_{soln})$) of Cd, Cu, Ni, Pb and Zn predicted by WHAM-VII against measured values for MA (●) and Urban (Δ) soils suspended in 0.01 M $Ca(NO_3)_2$ (1 g: 30 mL). M_E was used as the input variable for reactive metal concentration. The solid line represents the 1:1 relation, and the dashed lines represent ± 1 RSD for the model. Values of RSD and correlation coefficients (r) are also shown.

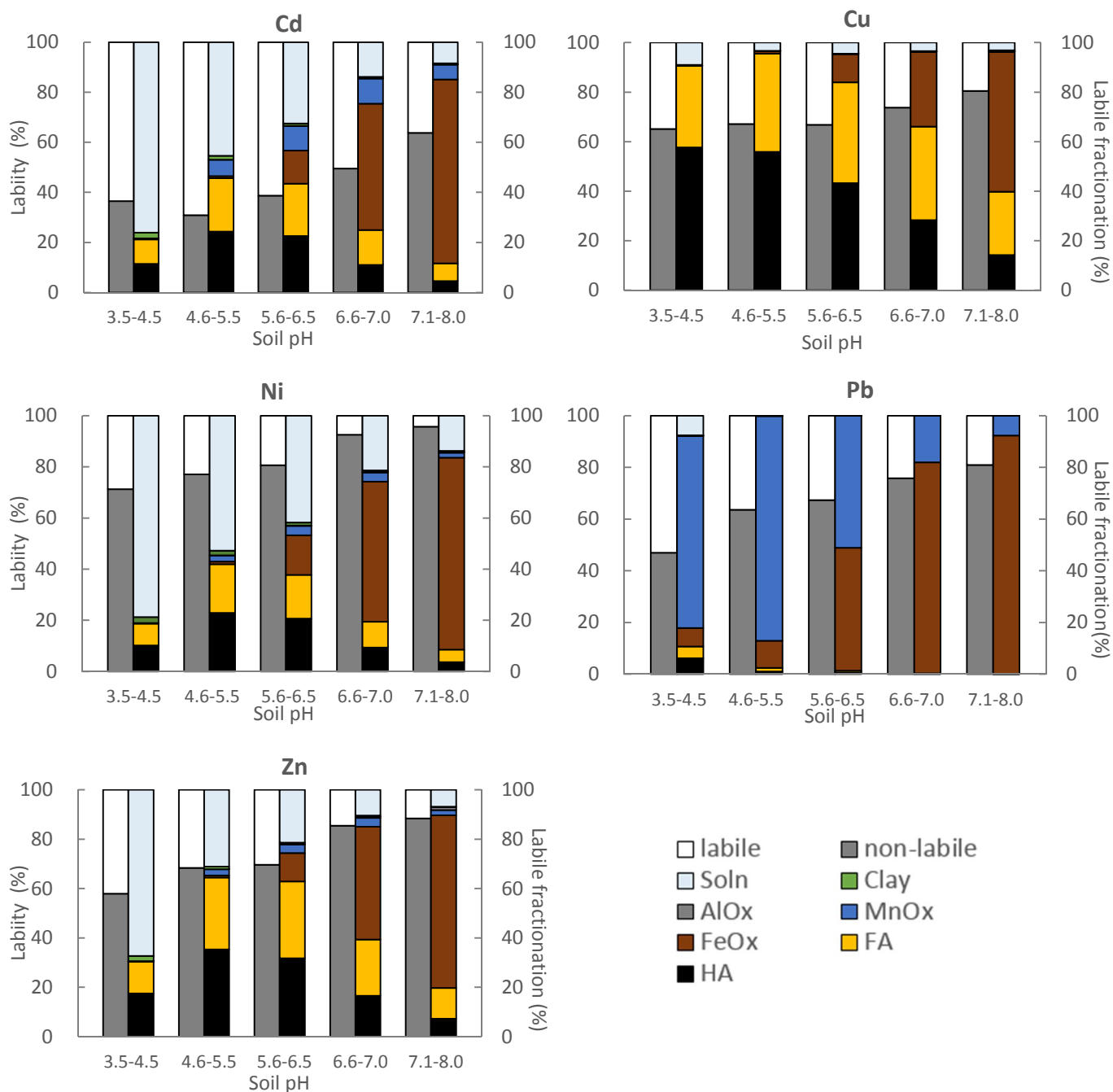


Figure 6: The first column shows fractionation by isotopic exchange into labile and non-labile metal (Cd, Cu, Ni, Pb and Zn) as a % of total soil metal content in MA (n=23) and Urban (n=50) soils, grouped by pH class. The second column shows the predicted distribution of the labile metal, only, between particulate humic and fulvic acid (HA and FA), Fe, Mn and Al oxides (FeOx, MnOx and AlOx), clays and the solution phase (Soln). Fractionation of labile metal was predicted using WHAM-VII parameterized using M_E as input (Appendix 1).

Appendix 1: Summary of the variables, parameters and settings for WHAM-VII modelling of trace metal solution concentration, speciation and fractionation.

| Variable | Settings |
|--|---|
| <i>Suspension condition</i> | |
| Suspended particulate matter (SPM) | 33.33 g L ⁻¹ |
| Temperature (K) | 288.15 K (15°C) |
| PCO ₂ (atm) | Measured bicarbonate concentration (DIC) |
| Soil pH | Measured in 0.01 M Ca(NO ₃) ₂ soil suspensions. |
| Charge balance options | No charge balance imposed i.e. a fixed (measured) pH value was used |
| <i>Adsorption phase (g L⁻¹)</i> | |
| Clay content | MA soils: estimated from soil texture Urban soils: measured by laser granulometry |
| Fe, Al and Mn oxides | DCB extraction; converted to Fe ₂ O ₃ .H ₂ O, Al ₂ O ₃ and MnO ₂ |
| Humic and fulvic acid | Measured by alkaline extraction |
| Colloidal fulvic acid | Estimated from measured DOC |
| <i>Major cation and anion concentration (mol L⁻¹)</i> | |
| Dissolved major cations (Na, Mg, Al, K and Ca) | Concentration in filtered soil suspensions (0.01 M Ca(NO ₃) ₂) <i>Precipitation option for Al:</i> One mole of precipitated Al(OH) ₃ forms 87 g of the binding phase within the particulate soil phase. |
| Fe ³⁺ activity | <i>Precipitation option for Fe:</i> assumes that Fe ³⁺ activity is controlled by Fe(III)(OH) ₃ solubility, calculated within the model. |
| Dissolved nitrate (NO ₃ ⁻) | Solution concentration estimated as 0.02 M in the suspension |
| Total dissolved carbonate (all species) | Estimated from total inorganic carbon measured in solution |
| <i>Trace reactive metal concentration in soil suspension (mol L⁻¹)</i> | |
| Total concentration Ni, Cu, Zn, Cd and Pb | Estimated from E-values (ME) |
| <i>Other settings</i> | |
| Activity coefficient correction | Debye-Hückel |
| WHAM parameter data sets | Default master, solute and binding phase data bases. |

Appendix 2 a): Summary of soil properties and total Ni, Cu, Zn, Cd and Pb concentration following metal amendment in MA soils.

| Soil series* | pH | SOC % | FeOx g kg ⁻¹ | MnOx g kg ⁻¹ | AlOx g kg ⁻¹ | Clay % | Total Ni mg kg ⁻¹ | Total Cu mg kg ⁻¹ | Total Zn mg kg ⁻¹ | Total Cd mg kg ⁻¹ | Total Pb mg kg ⁻¹ | DOC* mg L ⁻¹ |
|--------------|------|----------|----------------------------|----------------------------|----------------------------|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------|
| Bardsey | 3.57 | 3.18 | 19.9 | 0.16 | 1.44 | 35.0 | 69.6 | 134 | 273 | 2.5 | 343 | 48.1 |
| Wick | 3.76 | 4.47 | 17.9 | 0.22 | 1.26 | 10.0 | 82.1 | 158 | 327 | 2.7 | 346 | 58.1 |
| Iveshead | 3.79 | 6.55 | 16.3 | 0.20 | 2.99 | 5.0 | 73.8 | 147 | 328 | 3.1 | 345 | 46.0 |
| Pwelliperian | 4.69 | 3.03 | 14.6 | 0.47 | 3.44 | 35.0 | 97.7 | 161 | 498 | 3.1 | 341 | 26.0 |
| Rivington | 5.27 | 3.36 | 10.4 | 0.40 | 0.65 | 5.0 | 71.1 | 133 | 324 | 2.9 | 311 | 29.7 |
| Braunshweig | 5.36 | 2.28 | 5.4 | 0.61 | 0.10 | 15.0 | 73.3 | 138 | 318 | 2.8 | 292 | 18.0 |
| Woburn | 5.61 | 1.00 | 20.1 | 0.24 | 0.24 | 5.0 | 76.5 | 136 | 287 | 2.7 | 294 | 15.4 |
| Fladbury | 5.67 | 4.66 | 24.8 | 0.86 | 0.94 | 70.0 | 111 | 155 | 385 | 3.3 | 328 | 21.9 |
| Ticknall | 5.72 | 5.20 | 20.9 | 0.48 | 1.76 | 15.0 | 86.9 | 150 | 437 | 3.0 | 572 | 16.6 |
| Cottam | 5.76 | 2.08 | 15.6 | 0.61 | 0.67 | 15.0 | 92.1 | 161 | 365 | 3.5 | 332 | 12.9 |
| Rosemaund | 5.84 | 1.86 | 10.8 | 0.74 | 0.56 | 35.0 | 124 | 153 | 351 | 2.9 | 297 | 9.9 |
| Arrow | 6.06 | 2.08 | 15.9 | 0.57 | 0.64 | 10.0 | 83.1 | 156 | 347 | 3.2 | 323 | 10.3 |
| Watlington | 6.11 | 1.24 | 18.2 | 0.81 | 0.22 | 10.0 | 88.5 | 146 | 335 | 3.1 | 304 | 13.1 |
| Insch | 6.20 | 4.13 | 27.4 | 0.78 | 7.38 | 17.5 | 79.2 | 140 | 293 | 2.8 | 268 | 29.4 |
| Newport | 6.31 | 1.03 | 15.8 | 0.51 | 0.55 | 10.0 | 83.3 | 157 | 350 | 2.9 | 314 | 13.5 |
| Gleadthorpe | 6.45 | 1.68 | 8.8 | 0.35 | 0.41 | 10.0 | 75.2 | 145 | 341 | 3.0 | 306 | 13.8 |
| Denchworth | 6.78 | 4.42 | 18.9 | 0.77 | 1.07 | 70.0 | 98.0 | 155 | 316 | 2.8 | 300 | 10.8 |
| Ragdale | 6.78 | 4.10 | 29.8 | 0.79 | 1.60 | 35.0 | 107 | 154 | 404 | 3.3 | 321 | 13.3 |
| Bridgets | 6.91 | 2.38 | 28.7 | 2.68 | 3.01 | 35.0 | 108 | 142 | 377 | 4.3 | 306 | 7.1 |
| Marian | 6.95 | 7.06 | 15.8 | 2.54 | 0.15 | 35.0 | 93.6 | 172 | 417 | 3.2 | 377 | 16.3 |
| Worcester | 7.08 | 2.88 | 15.4 | 0.79 | 0.00 | 35.0 | 124 | 166 | 436 | 3.3 | 339 | 5.2 |
| Hanslope | 7.08 | 4.39 | 27.6 | 0.77 | 1.41 | 35.0 | 93.6 | 139 | 360 | 2.9 | 285 | 16.2 |
| Evesham | 7.12 | 2.38 | 22.0 | 0.98 | 1.11 | 70.0 | 97.6 | 155 | 337 | 3.0 | 312 | 7.6 |

*Soil Survey of England and Wales classification of soil series.

**DOC determined in suspension (1 g soil: 30 mL water).

Appendix 2 b): Summary of soil properties, sampling location, land use and total Ni, Cu, Zn, Cd and Pb concentration in Urban soils (Wolverhampton).

| Sample | pH | SOC % | FeOx g kg ⁻¹ | MnOx g kg ⁻¹ | AlOx g kg ⁻¹ | Clay % | Total Ni mg kg ⁻¹ | Total Cu mg kg ⁻¹ | Total Zn mg kg ⁻¹ | Total Cd mg kg ⁻¹ | Total Pb mg kg ⁻¹ | DOC* mg L ⁻¹ | Grid Ref. | Landuse |
|--------|------|----------|----------------------------|----------------------------|----------------------------|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------|---------------|----------------------------------|
| WV1 | 4.63 | 3.43 | 8.4 | 0.24 | 0.81 | 20.4 | 18.3 | 35.4 | 134 | 0.4 | 56.7 | 35.8 | 391030 301170 | Grassland (golfcourse) |
| WV2 | 3.92 | 2.81 | 9.7 | 0.44 | 1.08 | 22.5 | 12.1 | 19.4 | 61.5 | 0.3 | 53.2 | 40.6 | 388450 300860 | Grassland (golfcourse) |
| WV3 | 6.11 | 10.99 | 18.2 | 1.26 | 1.59 | 15.7 | 55.3 | 403 | 1050 | 3.7 | 266 | 59.4 | 393690 297700 | Park |
| WV4 | 5.87 | 3.35 | 13.8 | 0.46 | 1.07 | 19.8 | 22.9 | 69.1 | 313 | 0.6 | 109 | 23.0 | 392180 297280 | Grassland (open land) |
| WV5 | 6.46 | 13.28 | 26.3 | 0.84 | 1.16 | 14.6 | 77.9 | 233 | 588 | 1.3 | 227 | 8.0 | 393730 296530 | Old industrial (gas works) |
| WV6 | 6.84 | 9.81 | 38.5 | 1.52 | 2.50 | 18.6 | 300 | 2200 | 4170 | 26.1 | 746 | 8.0 | 394490 295160 | Wasteland (old landfill) |
| WV7 | 7.41 | 5.40 | 23.1 | 0.67 | 0.88 | 16.9 | 83.3 | 493 | 1170 | 3.6 | 590 | 3.2 | 394960 295960 | Grassland |
| WV8 | 5.64 | 10.07 | 19.7 | 0.92 | 4.47 | 16.4 | 57.4 | 158 | 553 | 2.1 | 358 | 17.7 | 397060 296980 | Woodland |
| WV9 | 5.56 | 4.39 | 16.8 | 0.62 | 1.66 | 18.4 | 32.3 | 134 | 300 | 0.9 | 273 | 17.5 | 390170 301290 | Grassland |
| WV10 | 7.07 | 8.01 | 19.9 | 0.84 | 0.94 | 18.3 | 66.9 | 298 | 1100 | 4.1 | 1050 | 9.7 | 391330 301090 | Old industrial (tyre factory) |
| WV11 | 4.46 | 3.68 | 14.9 | 0.38 | 1.80 | 22.9 | 25.3 | 87.7 | 514 | 1.9 | 173 | 28.9 | 390810 296710 | Domestic garden |
| WV12 | 5.79 | 2.73 | 11.1 | 0.51 | 0.75 | 18.9 | 15.0 | 30.4 | 270 | 0.7 | 199 | 22.9 | 388240 295750 | Grassland |
| WV13 | 5.54 | 3.83 | 12.6 | 0.64 | 0.71 | 24.4 | 25.4 | 51.1 | 308 | 1.0 | 131 | 22.1 | 392760 295760 | Park |
| WV14 | 5.22 | 25.08 | 20.3 | 0.55 | 0.68 | 5.1 | 58.4 | 265 | 1190 | 5.1 | 332 | 16.2 | 392830 299710 | Nature reserve (railway) |
| WV15 | 7.12 | 11.17 | 19.2 | 3.01 | 0.55 | 11.8 | 47.6 | 101 | 290 | 1.1 | 140 | 24.7 | 388910 299580 | Nature reserve (railway) |
| WV16 | 4.01 | 14.46 | 7.1 | 0.27 | 5.10 | 16.8 | 29.1 | 89.1 | 135 | 0.7 | 88.4 | 18.0 | 392380 295460 | Vegetated colliery spoil heap |
| WV17 | 5.64 | 2.76 | 11.1 | 0.52 | 0.87 | 19.4 | 26.9 | 73.8 | 239 | 0.6 | 141 | 50.3 | 391240 297580 | Old industrial (disused factory) |
| WV18 | 4.63 | 5.49 | 16.7 | 0.51 | 2.49 | 22.6 | 39.8 | 204 | 524 | 1.7 | 150 | 26.3 | 395120 299290 | Grassland (not maintained) |
| WV19 | 5.37 | 5.19 | 12.6 | 0.41 | 0.01 | 19.1 | 45.8 | 58.7 | 192 | 0.5 | 48.7 | 11.6 | 395150 299140 | Grassland |
| WV20 | 4.14 | 4.54 | 10.8 | 0.25 | 2.36 | 15.3 | 15.1 | 77.6 | 105 | 0.5 | 85.7 | 30.4 | 396720 301130 | Grassland |
| WV21 | 6.41 | 2.85 | 13.5 | 0.48 | 0.00 | 24.0 | 54.5 | 48.7 | 102 | 0.2 | 31.9 | 7.8 | 393960 299860 | Brownfield |
| WV22 | 8.08 | 2.50 | 12.3 | 0.35 | 0.00 | 21.3 | 43.1 | 90.0 | 154 | 0.3 | 45.9 | 7.3 | 394390 299860 | Brownfield |
| WV23 | 7.63 | 1.37 | 12.8 | 0.29 | 0.02 | 19.0 | 65.6 | 79.0 | 267 | 0.7 | 78.8 | 19.4 | 395400 299670 | Brownfield |
| WV24 | 7.22 | 2.64 | 14.1 | 0.45 | 0.43 | 21.1 | 33.6 | 82.3 | 605 | 1.2 | 351 | 12.3 | 394680 299830 | Brownfield |
| WV25 | 4.05 | 11.36 | 20.1 | 0.70 | 3.84 | 13.8 | 55.2 | 188 | 356 | 1.8 | 217 | 20.7 | 394210 298970 | Grassland (park) |
| WV26 | 6.60 | 2.70 | 9.9 | 0.28 | 0.00 | 20.6 | 20.0 | 52.6 | 133 | 0.5 | 63.3 | 23.2 | 394600 298750 | Grassland |
| WV27 | 7.67 | 3.16 | 28.7 | 0.54 | 0.29 | 20.5 | 39.1 | 160 | 279 | 0.6 | 177 | 15.3 | 392800 298520 | Brownfield |
| WV28 | 7.25 | 5.85 | 21.1 | 0.44 | 0.66 | 18.8 | 44.8 | 150 | 281 | 0.6 | 156 | 10.6 | 391700 310630 | Brownfield |
| WV29 | 6.87 | 20.50 | 27.4 | 1.03 | 0.64 | 20.0 | 94.1 | 338 | 739 | 3.3 | 429 | 10.4 | 391680 300080 | Deciduous woodland |
| WV30 | 6.32 | 3.60 | 13.5 | 0.34 | 0.26 | 18.6 | 24.0 | 82.3 | 158 | 0.6 | 109 | 18.3 | 391780 300120 | Grassland (park) |

Appendix 2 c): Summary of soil properties, sampling location, land use and total Ni, Cu, Zn, Cd and Pb concentration in Urban soils (Nottingham).

| Sample | pH | SOC % | FeOx g kg ⁻¹ | MnOx g kg ⁻¹ | AlOx g kg ⁻¹ | Clay % | Total Ni mg kg ⁻¹ | Total Cu mg kg ⁻¹ | Total Zn mg kg ⁻¹ | Total Cd mg kg ⁻¹ | Total Pb mg kg ⁻¹ | DOC* mg L ⁻¹ | Grid Ref. | Landuse |
|--------|------|----------|----------------------------|----------------------------|----------------------------|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------|---------------|-------------------------------|
| NG1 | 4.75 | 5.00 | 40.6 | 1.67 | 3.81 | 24.6 | 49.5 | 51.4 | 340 | 1.8 | 194 | 29.9 | 455470 336660 | Grassland (football field) |
| NG2 | 5.52 | 4.77 | 14.9 | 0.86 | 2.33 | 28.7 | 24.4 | 50.0 | 229 | 1.1 | 412 | 18.6 | 455280 338770 | Churchyard |
| NG3 | 6.47 | 5.10 | 34.4 | 1.14 | 1.60 | 21.4 | 44.1 | 26.5 | 111 | 0.3 | 60.9 | 29.1 | 453760 341550 | School |
| NG4 | 6.29 | 5.25 | 18.8 | 0.49 | 1.24 | 18.3 | 37.1 | 224 | 881 | 2.5 | 1300 | 7.0 | 454700 343720 | Domestic garden |
| NG5 | 6.99 | 3.26 | 14.6 | 0.47 | 0.38 | 20.1 | 31.6 | 57.9 | 439 | 1.1 | 353 | 14.6 | 457360 342370 | Domestic garden |
| NG6 | 6.78 | 10.70 | 39.5 | 0.81 | 1.36 | 19.8 | 60.1 | 161 | 459 | 2.0 | 406 | 14.6 | 458720 339210 | Railway |
| NG7 | 7.00 | 5.31 | 21.4 | 0.85 | 0.88 | 18.8 | 59.0 | 129 | 359 | 1.5 | 385 | 13.0 | 458500 339110 | Grassland (imported) |
| NG8 | 4.15 | 7.90 | 38.2 | 1.32 | 4.52 | 18.0 | 62.6 | 65.2 | 374 | 1.6 | 352 | 63.5 | 459710 339170 | Grassland (racecourse) |
| NG9 | 6.27 | 4.81 | 14.6 | 0.38 | 1.50 | 20.5 | 28.2 | 47.6 | 169 | 0.6 | 205 | 14.5 | 453570 344310 | Vegetated colliery spoil heap |
| NG10 | 6.53 | 5.21 | 18.5 | 0.79 | 1.38 | 21.7 | 35.2 | 54.4 | 301 | 0.8 | 257 | 11.7 | 455170 342480 | Vegetated colliery spoil heap |
| NG11 | 7.25 | 8.56 | 25.3 | 1.30 | 1.83 | 14.8 | 228 | 1260 | 1690 | 2.1 | 1110 | 6.4 | 455770 338590 | Disused factory |
| NG12 | 7.38 | 13.49 | 43.0 | 2.31 | 3.32 | 12.1 | 380 | 3190 | 2520 | 5.6 | 1240 | 6.9 | 455760 338550 | Disused factory |
| NG13 | 7.02 | 1.28 | 15.6 | 0.35 | 0.03 | 20.7 | 20.3 | 26.0 | 26.0 | 0.1 | 18.5 | 8.0 | 453570 344210 | Grassland (amenity) |
| NG14 | 6.54 | 11.41 | 16.7 | 0.59 | 3.59 | 13.0 | 370 | 644 | 1740 | 38.2 | 600 | 22.4 | 464120 340530 | Sewage Farm |
| NG15 | 5.99 | 6.86 | 15.5 | 0.30 | 2.79 | 20.7 | 199 | 382 | 1020 | 19.2 | 337 | 21.1 | 464130 340810 | Sewage Farm |
| NG16 | 7.57 | 5.03 | 25.0 | 0.93 | 0.61 | 18.9 | 44.0 | 92.9 | 223 | 0.9 | 121 | 7.3 | 462830 340800 | Brownfield |
| NG17 | 6.34 | 18.25 | 27.7 | 1.06 | 1.33 | 11.6 | 99.0 | 274 | 634 | 1.1 | 1410 | 16.9 | 462770 340730 | Brownfield |
| NG18 | 6.78 | 3.35 | 22.2 | 1.13 | 0.60 | 20.1 | 43.7 | 35.7 | 216 | 1.4 | 79.2 | 11.2 | 462900 340700 | Brownfield |
| NG19 | 6.93 | 2.98 | 34.8 | 1.43 | 2.19 | 18.7 | 32.3 | 31.7 | 132 | 0.4 | 65.9 | 12.3 | 446800 339730 | Brownfield |
| NG20 | 6.68 | 3.00 | 31.0 | 0.70 | 1.01 | 24.0 | 32.2 | 52.9 | 299 | 0.7 | 90.0 | 19.6 | 447040 339240 | Brownfield |

Appendix 3: Average difference between %M_E and %M_{E_r} (ΔM_E), RSD, R², p-values for correlations between %M_E and %M_{E_r} and standard error of the mean for replicate estimates of %M_E and %M_{E_r}.

| | Ni | Cu | Zn | Cd | Pb |
|--|-------|-------|-------|-------|-------|
| ΔM_E | -0.14 | 1.76 | -0.52 | -0.35 | -1.59 |
| RSD | 0.79 | 4.84 | 28.22 | 0.13 | 15.49 |
| r | 0.999 | 0.997 | 0.973 | 0.997 | 0.963 |
| p-value | >0.05 | <0.01 | >0.05 | >0.05 | >0.05 |
| SE _{%M_E} | 0.371 | 0.873 | 1.218 | 2.167 | 1.216 |
| SE _{%M_{E_r}} | 0.468 | 0.666 | 0.636 | 1.189 | 1.854 |

Appendix 4: Linear regression model coefficients, RSD and r values for model prediction of %M_E. The regression (see Eq. 3) was parameterized from %M_E (mg kg⁻¹) measured on MA soils. Values in brackets are the % of total variance, *n.s* = not significant.

| | Constant | pH | %C | FeOx (g kg ⁻¹) | MnOx (g kg ⁻¹) | AlOx (g kg ⁻¹) | Clay (%) | Total metal content (mg kg ⁻¹) | RSD | r |
|-----------|----------|-------------------|-------|-------------------------------|-------------------------------|-------------------------------|-------------------|--|------|------|
| Ni | 176 | -14.7** (73.1) | -0.96 | 0.20* (10.8) | 0.90** (<0.10) | -4.42 | 0.02* (<0.10) | -0.55** (1.90) | 5.85 | 0.97 |
| Cu | 99.7 | -4.87* (25.5) | -1.20 | 0.38 | -1.34* (4.80) | -3.46* (24.7) | -0.01 | -0.13 | 5.20 | 0.83 |
| Zn | 180 | -14.6** (66.1) | 0.53 | 0.04* (5.5) | 1.49** (<0.10) | -4.68 | -0.19* (<0.10) | -0.13* (10.9) | 7.70 | 0.95 |
| Cd | 185 | -11.5** (63.2) | -0.39 | 0.12 | 3.10** (0.40) | -3.39 | 0.06 | -13.2** (7.70) | 6.30 | 0.92 |
| Pb | 75.9 | -7.02** (53.3) | -1.08 | 0.57 | -7.26** (8.20) | -0.76 | -0.01 | 0.06 | 6.91 | 0.85 |

** significant (p < 0.01), * significant (p < 0.05)

Appendix 5: Values of model parameters (pH_{50} , k_M , n), RSD, r values and $\Delta\%M_E$ (average deviation of predicted $\%M_E$ from measured value) from sigmoidal model prediction of $\%E$ -value using Eq. 4 and Eq. 5 applied to MA soils only. The values in bold italic are the best fit of the measured $\%M_E$.

| | | Ni | Cu | Zn | Cd | Pb |
|--------------------|---------------------------------|-------------|-------------|-------------|--------------|-------------|
| Equation 4: | | | | | | |
| | pH₅₀ | 5.06 | 5.55 | 5.36 | 7.89 | 6.33 |
| | k_M | 0.76 | 0.16 | 0.72 | 0.66 | 0.35 |
| | RSD | 11.5 | 7.59 | 13.2 | 8.73 | 8.97 |
| | r | 0.85 | 0.51 | 0.81 | 0.77 | 0.72 |
| | $\Delta\%M_E$ | -0.39 | -0.01 | 0.01 | 0.13 | 0.12 |
| Equation 5: | | | | | | |
| pH + %SOC | pH₅₀ | 4.94 | 5.17 | 5.02 | 7.59 | 6.27 |
| | k_M | 0.54 | 0.07 | 0.23 | 0.38 | 0.12 |
| | n | 0.28 | 0.57 | 0.95 | 0.86 | 0.86 |
| | RSD | 11.2 | 7.66 | 13.3 | 11.5 | 8.53 |
| | r | 0.86 | 0.50 | 0.81 | 0.65 | 0.76 |
| | $\Delta\%M_E$ | 0.18 | 0.66 | 1.43 | 0.37 | 0.74 |
| pH + Ox | pH₅₀ | 4.99 | 5.47 | 5.29 | 8.03 | 6.40 |
| | k_M | 0.16 | 0.06 | 0.12 | 1.19 | 0.13 |
| | n | 0.83 | 0.57 | 0.95 | -0.40 | 0.55 |
| | RSD | 10.4 | 7.45 | 12.3 | 8.06 | 8.80 |
| | r | 0.88 | 0.53 | 0.84 | 0.81 | 0.73 |
| | $\Delta\%M_E$ | 0.15 | 0.40 | 1.08 | 0.06 | -0.02 |
| pH + %Clay | pH₅₀ | 5.01 | 5.70 | 5.16 | 7.22 | 6.46 |
| | k_M | 0.20 | 0.03 | 0.03 | 0.10 | 0.02 |
| | n | 0.41 | 0.57 | 0.95 | 0.86 | 0.86 |
| | RSD | 10.0 | 7.17 | 14.5 | 11.8 | 11.4 |
| | r | 0.89 | 0.58 | 0.77 | 0.65 | 0.51 |
| | $\Delta\%M_E$ | 1.05 | 0.12 | 2.75 | 0.19 | 2.04 |

Appendix 6: Summary of model outcomes comparing predicted and measured solution concentrations of Ni, Cu, Zn, Cd and Pb using E-values (M_E) as input variables to WHAM-VII (Appendix 1; Fig. 5).

| | Ni | Cu | Zn | Cd | Pb |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|
| RSD | 0.51 | 0.45 | 0.83 | 0.63 | 0.64 |
| r | 0.94 | 0.74 | 0.94 | 0.94 | 0.85 |
| $\Delta p(M)$ | 0.40 | 0.23 | 0.58 | 0.56 | -0.02 |
| slope | 0.82 | 0.73 | 0.54 | 0.78 | 0.80 |
| intercept | 0.77 | 1.53 | 2.08 | 1.11 | 1.70 |

Appendix 7 a): Correlation (r) between ΔpM_{soln} (the bias between measured and modelled solubility by WHAM on a $-\log$ scale) and soil pH or percentage binding with an important particulate phase (FeOx, MnOx, AlOx, HA) or colloidal (dissolved) phase (FA).

| r | Ni | Cu | Zn | Cd | Pb |
|---------------------|--------------|---------------|--------------|--------------|----|
| pH ($p < 0.01$) | 0.431 | 0.354 | 0.751 | 0.749 | |
| FeOx ($p < 0.05$) | <i>0.284</i> | | <i>0.744</i> | <i>0.532</i> | |
| MnOx ($p < 0.05$) | <i>0.270</i> | <i>0.342</i> | | | |
| HA ($p < 0.05$) | | <i>-0.414</i> | | | |
| Colloidal-FA | | <i>0.510</i> | | | |

Appendix 7 b): Difference between measured and predicted Pb solubility (ΔpPb_{soln}) as a function of (a) soil pH and fractional sorption by (b) FeOx and (c) MnOx.

